CHAPTER THIRTY-SEVEN

RADIOCARBON DATING OF POTTERY FOOD CRUSTS: RESERVOIR EFFECT OR NOT? THE CASE OF THE SWIFTERBANT POTTERY FROM DOEL "DEURGANCKDOK" (BELGIUM)

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Abstract

In order to verify the relative dating of the Swifterbant pottery collected at the Final Mesolithic site of Doel "Deurganckdok"- dating based on morphology and decoration - a series of direct dates were obtained on samples of food crusts preserved on the inner surface of numerous potsherds. In addition a number of indirect dates were done on samples of organic material and cremated bones originating from presumed surface hearths. The results indicate an important incompability between the food crust dates and the other dates, the former being systematically older. This incompability may be explained by a reservoir effect of the food crusts, caused by the processing of (freshwater) fish.

Gas chromatography mass spectrometry of lipids, present in the food crust, is an interesting analytical tool to obtain information about the cooked ingredients in the pottery. The application of this technique in combination with EA-IRMS can not prove with 100% reliability the presence of aquatic products in food crusts of pottery. Hence for the moment direct dating of food crusts remains problematic.

Résumé

La datation relative de la céramique Swifterbant, recueillie au site mésolithique final à Doel "Deurganckdok" - datation basée sur la morphologie et la décoration – est vérifiée par une série de dates directes tirées des échantillons de résidus alimentaires déposés sur la paroi intérieure de bon nombre de tessons. En plus, plusieurs dates indirectes ont été retirées de matières organiques et d'ossements incinérés. Les résultats indiquent une incompatibilité importante entre les dates des résidus alimentaires et les autres dates, les premières se révélant systématiquement plus anciennes. Un effet réservoir sur les résidus alimentaires provoqué par le traitement de poisson d'eau douce pourrait figurer comme explication.

La chromatographie en phase gazeuse couplée avec un spectromètre de masse des lipides, présents dans les résidus alimentaires, est un technique analytique intéressante pour obtenir de l'information des denrées alimentaires qui ont été cuites dans les céramiques. L'application de cette technique combinée avec EA-IRMS n'est pas capable de prouver à 100% la présence des produits aquatiques dans les résidus alimentaires. Ainsi la datation directe des résidus alimentaires demeure problématique.

Keywords*: food crusts, reservoir effect, radiocarbon dating, gas chromatography mass spectrometry (GC-MS), elemental analysis isotope ratio mass spectrometry (EA-IRMS)*
Mots-clés*: résidus alimentaires sur tessons de céramique, effet réservoir, datation au radiocarbone, chromatographie en phase gazeuse couplée avec un spectromètre de masse (GC-MS), analyseur élémentaire couplé à un spectromètre de masse à ratio isotopique (EA-IRMS).*

1. Introduction

Direct radiocarbon dating of charred food crusts has become more popular in archaeology. This type of material is in direct association with the use of the pottery and cannot be a material intrusion. Hence it is generally expected that food crusts yield reliable radiocarbon dates. However, Fischer and Heinemeier (2003, 449-466) noticed that some food crust dates from Scandinavian Late Mesolithic sites are older than the dates obtained on terrestrial organic material and their archaeological context, suggesting that a reservoir effect caused by the processing

of fish might be implicated.

Lipid analysis of charred deposits, preserved on the inner surface of potsherds, is now an interesting technique to obtain information about the cooking and diet habits. By the use of different techniques (GC, GC-MS, LC-MS,GC-C-IRMS) certain plant products and animal fats can be identified and distinguished (Dudd, Regert and Evershed 1998, 1999; Romanus et al. 2007). Despite this, the evidence of the presence of aquatic products in food crusts still remains problematic. This will be demonstrated in this paper using data from two Final Mesolithic wetland sites situated in NW Belgium.

2. Materials and techniques

2.1 Sample selection

Archaeological surveys during the construction of a new dock, the "Deurganckdok" at Doel, situated in the Antwerp harbour along the Lower Scheldt (Crombé 2005; Sergant, Crombé and Perdaen 2006), led to the discovery of three wetland sites yielding pottery of Swifterbant tradition in association with Final Mesolithic, hunter-gatherer-fisher settlement remains (lithics, burnt ecofacts, etc.). Stylistically, the pottery closely resembles the Early Swifterbant pottery from the Netherlands, dated to the first half of the 5th millennium cal BC.

Surface residues from potsherds were obtained from two of these wetland sites, Doel-sector B and Doel-sector J/L. Faunal remains, namely burnt freshwater fish bones, mainly belonging to cyprinids, and cremated wild animal bones from red deer and wild boar were also found on these sites. Among the carbonised seeds and fruits, several edible species occur, such as hazelnuts, crab apples, sloes, acorns and hawthorn berries (Crombé 2005).

2.2 Extraction

The food crusts were removed using a scalpel and crushed to a fine powder in a mortar with a pestle. Between 0.1-0.5g of each sample was ultrasonically extracted with a 30ml mixture of chloroform and methanol (2:1 v:v) for 30 minutes and filtrated afterwards. The solvent was partially evaporated and the remaining solvent was removed under a stream of nitrogen. The dried total lipid extracts were stored in the freezer for further analysis.

2.3 Derivatisation

The lipid residues were treated with 50µl of a mixture benzene/MethPrep 2 (*m*-trifluoromethylphenyl) trimethylammonium hydroxide, Alltech) to release fatty acid methyl esters (FAMEs) for one hour at 60°C .

2.4 Gas Chromatography/Mass Spectrometry

For analysis, 1µl of the derivatisated extract was injected on a Trace gas chromatograph ultra coupled to a Finnigan Polaris Q mass spectrometer.

The gas chromatograph is equipped with a AT5-MS column (Alltech, 30m*0.25mm and 5m uncoated guard column). The injection was done split or splitless, depending on the total lipid extract yield, at 280°C. The oven temperature was held at 65°C for 1 minute, then increased to 100°C at 30°C/min and from 100°C to 290°C at 4°C/min and finally an isothermal 12min hold at 290°C. Helium was used as carrier gas and held at a constant flow of 1.3ml/min.

The gas chromatograph was connected to the mass spectrometer via an interface with a constant temperature of 290°C. The fragmentation of the separated compounds was done by electronic ionisation (EI). The temperature of the ion source was 220°C. The mass filter was set to scan between m/z 50 and 600.

2.5 Stable carbon and nitrogen isotope analysis of bulk

$\delta^{13}C$ and $\delta^{15}N$, atomic C/N measurements were made on a number of the bulk residue samples (Table 37-1). Acid-Alkali-Acid pre-treatment of the samples, to remove carbonates, humic and fulvic acids, was undertaken prior to analysis. Each sample was transferred in duplicate into tin capsules and was analysed using a ThermoFinnigan delta +XL (continuous flow type), interfaced with a Flash EA1112 elemental analyser via a Conflo III interface. Both elements were measured together and a Helium-dilution was applied for carbon as the amount of C in the crusts was often far in excess of the amount of N. Analytical precision was greater than 0.5‰ for both elements, as determined by duplicate measurements.

2.6 Radiocarbon dating

In order to verify the relative dating an extensive radiocarbon dating program was set up, aiming at dating different materials from the same stratigraphic and

spatial context. Direct dates were obtained on samples of food crusts preserved on the inner surface of numerous potsherds, while indirect dates were done on samples of carbonised hazelnut shells, charcoal, burnt seeds and cremated bones originating from presumed surface hearths (Crombé 2005, 180-212).

3. Fish identification

Many attempts have already been done to find a lipid biomarker for aquatic products in ceramic vessels. None however has proven to be conclusive.

Nervonic acid, C24:1 can be an indication for marine fish (Patrick, De Koning and Smith 1985, 231-236) but it's also a major constituent in seed oils of brassica.

The detection of a group unsaturated fatty acids, C16:1, C20:1 en C22:1, in a food crust can indicate fish consumption (Brown and Heron 2003, 35-41). These three biomolecules however are not biomarkers for fish. C16:1 and C20:1 were both detected in other vegetable and animal sources and C22:1 is only observed in marine fish oils but not in freshwater fish (Morgan et al. 1983, 356-360); it has also been found in some seed oils (Rossell 1990, 261-327).

Fischer and Heinemeier (2003, 449-466) suggested that stable carbon isotope ratio heavier than -26 ‰ are of marine origin and lighter than -26 ‰ of freshwater origin.

Hansel et al. (2004, 2999-3002) identified W-(o-alkylphenyl)alkanoic acids with 16, 18 and 20 carbon atoms, formed via alkali isomerization, during heating of triunsaturated fatty acids C16:3, C18:3, C20:3. The presence of these ω-(o-alkylphenyl)alkanoic acids, together with the isoprenoid fatty acids (4,8,12-trimethyltridecanoic acid (4,8,12-TMTD) and 3,7,11,15-tetramethylhexadecanoic acid (phytanic acid)), typical for marine animals (Akman and Hooper 1968, 549-565) and a dominant C16:0 peak can be used as biomarkers for fish (Hansel et al. 2004, 2999-3002).

Passi et al. (2002, 7341-7322) however have pointed out that C16:3 and C18:3 alkanoic acids are common constituents in vegetable oils and marine fish oils, while the C20:3 alkanoic acid is only observed in marine fish oils.

Phytanic acid was detected in river sediment (Maxwell et al. 1973, 297-313). The fatty acid 4,8,12-TMTD and phytanic acid are degradation products from phytol in aquatic environments (Rontani and Volkman 2003, 1-35). This proves that these two components can be from marine or freshwater origin. Theoretically,

these two degradation products of phytol could be formed in terrestrial environment but we are not aware of any studies. But lipids of bovine tissues and milk showed the presence of phytanic acid too (Lough 1977, 115-119).

A typical degraded plant lipid distribution is the C16:0 peak dominating significantly that of C18:0 (Copley et al. 2001, 538-542). Ollson (2004) however proved through decomposition experiments that it is impossible to separate fish from plant lipid residues mainly because the n-alkanoic acid distribution of both is dominated strongly by the C16-acid. If a dominated C16:0 peak is detected in the chromatogram, together with cholesterol and sitosterol, it may indicate a mixed diet of mainly vegetables and fish.

To distinguish aquatic products Craig et al. (2006, 135-152) used the presence of ω-(o-alkylphenyl)alkanoic acids C16:3, C18:3, C20:3, secondly the stable isotopes of individual lipid compounds associated with archaeological sherds by gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) and the bulk isotopes ($\delta^{15}N$ and $\delta^{13}C$) of the charred residues. Nitrogen isotope values were plotted against carbon isotope values for each sample. Three groups of samples can be nominally discriminated. The first group has relatively heavy $\delta^{13}C$ values (>-25‰) and $\delta^{15}N$ values between +7 and +12‰ which suggest a marine origin. The second group has relatively light $\delta^{13}C$ values (<-25‰) and $\delta^{15}N$ values between +6 and +10‰. It is suggested that freshwater fish is a likely component of these residues, and probably the major component for samples with high $\delta^{15}N$ (+8 and +10‰). The last group has light $\delta^{13}C$ values (<-25‰) and $\delta^{15}N$ values between +1 and +5‰ and herbivore products and/or plant material was processed in these pots (Craig et al. 2006, 135-152).

The analysis of stable carbon isotopes of individual alkanoic acids by gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) is useful to identify ruminant adipose fat (Romanus et al. 2007, 729-747) but seems not able to separate marine and porcine lipids, or to separate between freshwater fish and terrestrial mammals (Craig et al. 2006, 135-152).

Olson and Isaksson (2007) defined the following criteria to identify possible fish residues: Firstly the peak-area ration C18:0/C16:0 < 0.48 or C16:0/C18:0 > 2.06, as observed from experimentally decomposed lipid data (Isaksson 2000; Ollson 2004) together with the presence of cholesterol, and/or the presence of the two acyclic isoprenoid alkanoic acids and the complete set of C16:3, C18:3 and C20:3 ω-(o-alkylphenyl)alkanoic acids. The C16:0/C18:0-proxy can be applied when no plant material was cooked in the pottery as plant material has a dominant palmitate peak. Sitosterol, a plant lipid biomarker, was detected in the Doel food

crust samples and the use of the C16:0/C18:0 peak area ratio was excluded.

Based on these observations and experiences, our criteria for determining fish processing in the Doel vessels was the presence of C20:3 ω-(o-alkylphenyl)alkanoic acid and the bulk stable isotopes theory, proposed by Craig et al. (2006, 135-152).

4. Results and discussion

4.1 Radiocarbon dating

In total 18 food crust samples, 16 from sector B and 2 from sector J/L, have been dated (Table 37-1). In addition 8 samples consisting of charcoal, carbonised hazelnut shells and seeds were also dated (Table 37-3).

All these dates are calibrated and plotted in figure 37-1 using Oxcal 3 (calibration curve: IntCal04). The food crusts, plotted in black, are clearly older than the plant material, plotted in grey. Only food crusts 416 (KIA-33811, 5685±40 BP), 281 (KIA-33820, 5665±40 BP) and 304 (KIA-29788, 5595±40 BP) have radiocarbon dates which overlap with the dates on plant remains.

Next the quartile interval and sum probability of the food crusts and plant material were calculated (calib 5.0) (Fig. 37-2; Table 37-2). KIA-29788 is considered as an outlier: the radiocarbon date is smaller than Q1-(Q3-Q1)*1.5 and Q1 is the first quartile and Q3 is the third quartile (Moore and McCabe 2006). There is a small overlap but the flourishing periods of both materials – food crusts and plants - are clearly different. The mean age difference is 320±159 BP as calculated with the data from table 37-3.

This difference is of the same order as the one calculated at the Dutch site of Molenaarsgraaf burial II (240±65 BP) on the basis of charcoal and human bone collagen (Lanting and van der Plicht 1996, 491-519). Based on the $\delta^{13}C$ value of the human bone collagen (-22.55 and -22.60‰) it was concluded that the person dated from this site had been consuming fish. Hence the age difference probably reflects a reservoir effect due to the consumption of fish. Unfortunately no human bones were found at Doel, which might help us in clarifying the observed discrepancy between the food crust and plant dates. Hence we had to look for other ways to solve this dating problem.

Sample Code	Lab code ^{14}C date	^{14}C date (BP)	δ^{13}C (‰)	δ^{15}N (‰)	Atomic C/N	C20:3
SECTOR B						
3	*KIA-33819*	5865±40	-27.0	7.9	7.7	-
16		n.a.	-27.1	7.2	n.a.	-
86		n.a.	-28.5	7.3	16.6	+
87	*KIA-33815*	5820±45	-27.4	3.5	12.2	+
90		n.a.	-26.8	6.4	46.6	-
95		n.a.	n.a.	n.a.	n.a.	-
102		n.a.	-27.9	7.2	26.6	-
109	*KIA-12260*	5980±35	n.a.	n.a.	n.a.	n.a.
129		n.a.	-27.6	7.2	20.0	-
132		n.a.	-26.0	9.8	58.2	+
248		n.a.	-27.0	6.3	22.6	-
251	*KIA-33818*	5820±40	-26.7	4.1	13.0	n.a.
266		n.a.	-26.8	8.4	14.9	+
277	*KIA-33817*	5790±45	-28.2	8.8	12.2	n.a.
279	*KIA-33816*	5825±45	-27.3	4.5	n.a.	-
281	*KIA-33820*	5665±40	-28.4	3.7	n.a.	-
291	*KIA-29787*	5810±35	-27.2	2.8	n.a.	-
293		n.a.	-27.0	5.2	n.a.	-
294		n.a.	-27.8	6.2	11.2	n.a.
304	*KIA-29788*	5595±40	-27.3	6.3	n.a.	-
416	*KIA-33811*	5685±40	-26.7	8.3	n.a.	+
419	*KIA-29789*	5910±40	-27.0	8.5	n.a.	+
430	*KIA-33809*	5875±45	-27.4	5.7	13.0	n.a.
440	*KIA-33812*	5880±40	-26.5	6.7	n.a.	-
477		n.a.	-26.3	3.9	n.a.	-
550	*KIA-32599*	5780±40	-27.0	9.6	n.a.	+
742	*KIA-14399*	5835±35	n.a.	n.a.	n.a.	n.a.
1135		n.a.	n.a.	n.a.	n.a.	-
1180		n.a.	n.a.	n.a.	n.a.	-
2033 (1)		n.a.	n.a.	n.a.	n.a.	-
2033 (2)		n.a.	n.a.	n.a.	n.a.	-
W18Z2(3)		n.a.	-27.2	8.2	n.a.	n.a.
W24/Z2(4)	*KIA-20232*	6015± 30	n.a.	n.a.	n.a.	n.a.
SECTOR J/L						
J/L-46	*KIA-20207*	5900± 45	-27.3	7.7	n.a.	n.a.
J/L-62	*KIA-20233*	5915± 45	-28.3	8.8	n.a.	n.a.
J/L1		n.a.	-26.6	8.6	17.7	n.a.

Table 37-1: Analysed food crusts.

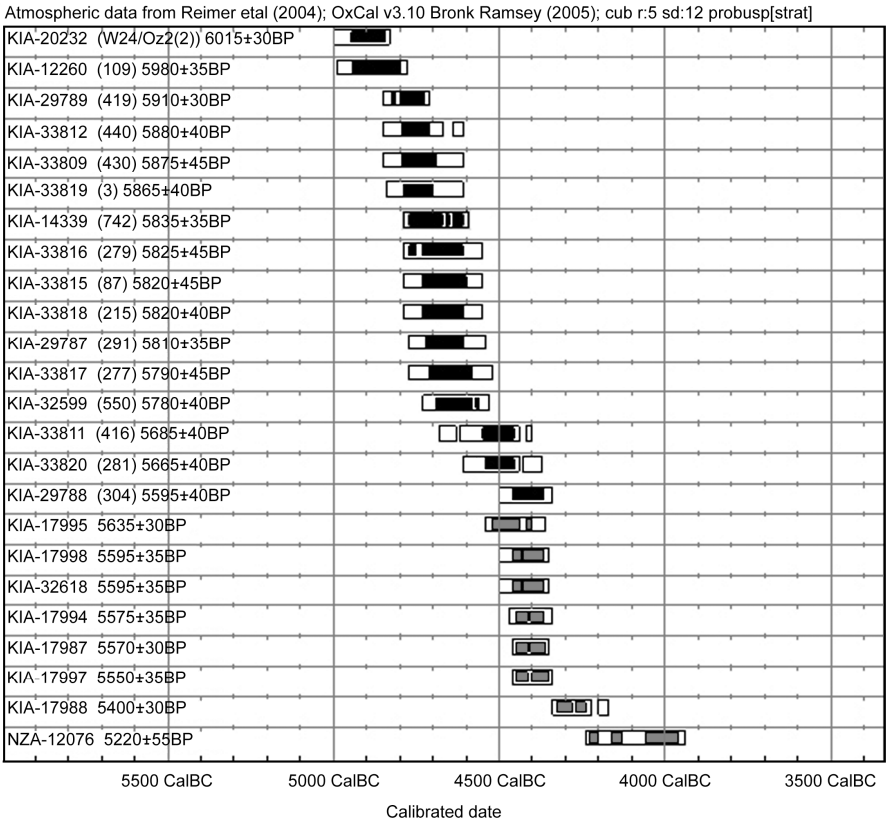

Fig. 37-1: Plot of radiocarbon dates.

radiocarbon dated material	2.50%	25% (Q1)	75% (Q3)	97.50%
Food crust	-4930	-4764	-4600	-4399
Organic material	-4500	-4435	-4334	-3990

Table 37-2: Quartile interval of food crusts and organic material.

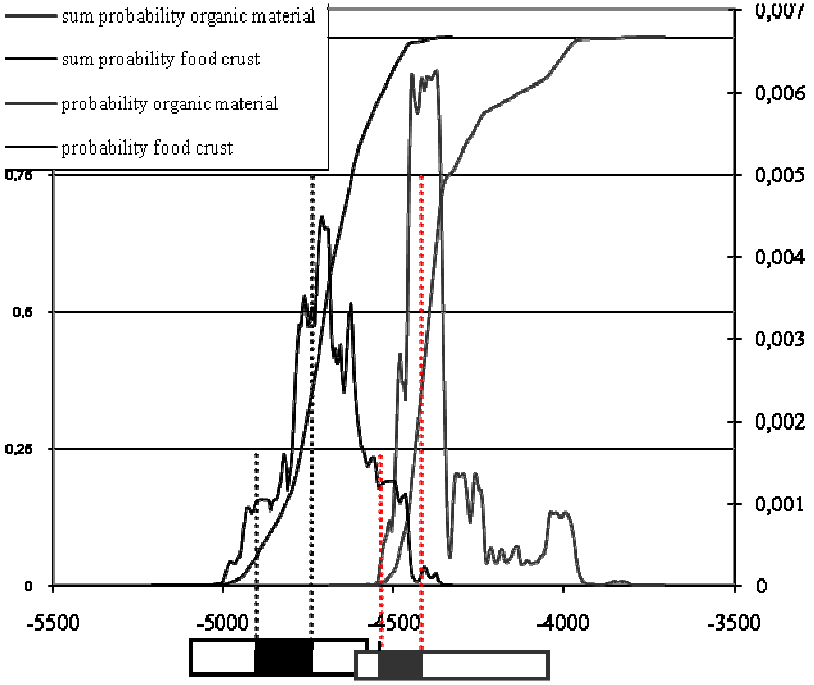

Fig. 37-2: Sum probability of food crusts and organic material.

Burnt mammal and fish bones, largely represented on the site of Doel-sector B, were chosen for these purposes. A selection of 9 samples, 7 consisting of mammal fragments and 2 of freshwater fish fragments, were radiocarbon dated (Table 37-4). It was hoped that a confrontation of both series of dates might allow us to determine the reservoir effect in a general way.

Among the dates from mammal bones KIA-31325 can be considered as an outlier, as the radiocarbon date falls outside Q3+(Q3-Q1)*1.5 (Moore and McCabe 2006). The later radiocarbon date of KIA-31322 could have been caused by the very small sample and is excluded for the calculation of the sum probability (Table 37-5). This caused problems during pre-treatment and graphitisation. The remaining mammal dates are in good agreement with the radiocarbon dates from carbonised plant material (Table 37-3 and 37-4), proving that the latter reliably date the Swifterbant occupation.

Food crust			**Organic material**		
Lab code ^{14}C date	**^{14}C date (BP)**	**stdev**	**Lab code ^{14}C date**	**^{14}C date (BP)**	**stdev**
KIA-20232	6015	30	*KIA-17995*	5635	30
KIA-12260	5980	35	*KIA-17996*	5595	35
KIA-14339	5835	35	*KIA-17994*	5575	35
KIA-29789	5910	30	*KIA-17987*	5570	30
KIA-29787	5810	35	*KIA-17997*	5550	35
KIA-32599	5780	40	*KIA-17986*	5400	30
KIA-33812	5880	40	*NZA-12076*	5220	55
KIA-33809	5875	45	*KIA-32618*	5595	35
KIA-33819	5865	40			
KIA-33816	5825	45			
KIA-33815	5820	45			
KIA-33818	5820	40			
KIA-33820	5665	40			
KIA-33811	5685	40			
KIA-33817	5790	45			
Average date (BP)	5837		**Average date (BP)**	5518	
Standard deviation	93		**Standard deviation**	139	

Table 37-3: Radiocarbon dated food crusts and organic material.

The dating results from the burnt fish bones on the other hand are disappointing. While it was expected that these dates would turn out to be (much) older than the mammal bone dates and plant dates, the results (KIA-31350 and KIA-31352) are unexpectedly late. Probably this can be explained by the fact that these small samples were not pre-treated sufficiently; hence their later radiocarbon dates are probably caused by later secondary carbonate coming from rain water. Dating of burnt bones is proven to be successful if large pieces (>2g) are available (Naysmith et al. 2007, 403-408). In the case of the Doel fish samples, only small pieces, varying from 20 to 200mg, were collected and added together to make radiocarbon dating possible. Pre-treatment with 1% acetic acid may be the solution to eliminate secondary carbonate contamination in small pieces of burnt bones (Van Strydonck, Boudin and De Mulder in press).

Lab code ^{14}C date	Sample code	^{14}C date (BP)	stdev	Weight before/after treatment (mg/mg)	mg graphite
Cremated mammal bone					
KIA-26465	*W18/Z1(2)*	5425	30	2780/ 1391.5	1.5
KIA-30960	*W19/Z2(1)*	5450	35	4050/ 2480	1.58
KIA-30981	*W16/Z7(2)*	5310	70	1469/682	1.01
KIA-31325	*W15/Z7 (4)*	6320	40	1880/940	0.35
KIA-31354	*W16/Z7(1)*	5680	40	1440/792	n.a.
KIA-31322	*W18/Z9(2)*	4885	55	1345/485	n.a.
KIA-31326	*W20/Z2(1) + W19/Z2(3)*	5355	45	940/495	0.15
Cremated fish bone					
KIA-31350	*W19/Z2(3) + Z2(4)+ Z2 (1)*	5130	40	no pretreatment	0.31
KIA-31352	*W15/Z7 (4) + Z7(4) + Z7(3)bis*	5150	50	no pretreatment	0.17

Table 37-4: Weight after pre-treatment and radiocarbon dates of cremated bones and yielded carbon after graphitisation.

4.2 Fish identification

4.3 Bulk isotopes and atomic C/N

So, if we apply the group discrimination mentioned by Craig et al. (2006, 135-152) as described above (cf. 3), all the radiocarbon dated food crusts with a δ^{13}C lighter than -25‰, which includes all the Doel samples, suggest freshwater fish consumption. The δ^{15}N values divide the Doel radiocarbon dated samples into two groups (Table 37-1; Fig. 37-3). The first, with ^{14}C-dated samples 3, 277, 304, 416, 419, 430, 440, 550, J/L-46, J/L-62, has δ^{15}N values between +6 and +10‰, which according to Craig et al. (2006) suggest that freshwater fish is a likely component of these residues, and probably the major component for samples with high δ^{15}N (+8 and +10‰). A second group, with ^{14}C-dated samples 87, 251, 279, 281, 291, has δ^{15}N values between +1 and +5‰ indicating the processing of mainly herbivore products and/or plant material in the pots (Craig et al. 2006, 135-152).

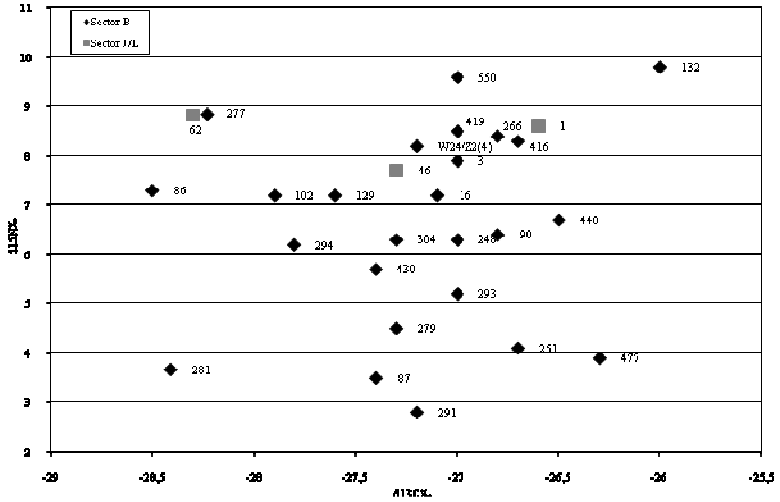

Fig. 37-3: Stable isotopes plot of food crusts.

The quartile interval of these two groups of food crusts is calculated (Fig. 37-4; Table 37-5). Theoretically a clear age difference should be expected between both groups. This is however not the case: both series of dates present the same flourishing period. The only difference is that group 1 (6‰< δ^{15}N<10‰) has an earlier start. Based on Craig's criteria (2006,135-152) the quartile interval of the food crusts from group 2 with δ^{15}N<5 should approach the quartile interval of the dated carbonised plant remains and mammal bones (Table 37-2 and 37-5). This is clearly not the case.

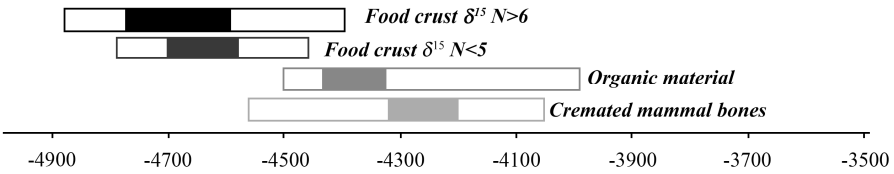

Fig. 37-4: Sum probability of food crusts, organic material and cremated mammal bones.

radiocarbon dated material	2.50%	25% (Q1)	75% (Q3)	97.50%
***Food crust* $d^{15}N > 6$**	-4870	-4772	-4598	-4386
***Food crust* $d^{15}N < 5$**	-4776	-4701	-4582	-4453
Organic material	-4500	-4435	-4334	-3990
Cremated mammal bones	-4575	-4332	-4195	-4038

Table 37-5: Sum probability of food crusts, organic material and cremated mammal bones.

Furthermore the $\delta^{15}N$ value of 8.3‰ of sample 416, for example, suggests freshwater fish as the major component of the residue. Yet the radiocarbon date (5685±40 BP) suggests a minimal or even no reservoir effect. In this particular case the $\delta^{15}N$ value could probably be explained by the consumption of wild boar, an omnivorous mammal.

Furthermore all food crusts have a $\delta^{13}C$ values lighter than -25‰ which, according to the literature, suggests freshwater fish consumption. But if plant material and fish products are cooked in the same pot, it will be difficult to distinguish these two products as the $\delta^{13}C$ for C3-plants fall into the range -34‰ to -22‰ (Vogel 1993, 29-46). To distinguish food products based on these facts, one has to conclude that the use of bulk stable isotopes of charred residues should be applied very carefully.

This is also suggested by the C/N of the Doel food crusts; these vary between 7.7 and 58.2 (Table 37-1). Microbial degradation (Dudd, Regert and Evershed 1998; Evershed et al. 1999), soil contamination and thermal degradation (De Niro and Hastor 1985; Spangenberg, Jacomet and Schibler 2006) can change the lipid concentration and also cause shifts in both stable isotopes which will complicate the reliable use of it. The main reason why bulk stable isotopes have to be used carefully is that the C/N ratio of the food crust is not in a certain range. For archaeological bones, the atomic C/N-ratio of the collagen should be between 3.2 and 3.6 in order to obtain reliable stable isotopes (De Niro 1985, 806-809). The effects of diagenesis on skeletal remains is fundamental to the interpretation of human dietary relationships and health through elemental and isotopic analysis of bone (Heron and Evershed and Goad 1991, 641-659) and the C/N-ratio is one of the parameters to measure the bone collagen quality (Van Strydonck, Boudin and Ervynck 2005, 369-376).

4.3.3 Gas Chromatography-Mass Spectrometry

GC-MS analysis detected C20:3 ω-o-alkylphenyl alkanoic acid in sample 87, 416, 419, 550 from the radiocarbon dated food crusts (Table 1). Sample 419 and 550 have a $\delta^{15}N$ value heavier than +6‰ and also an aberrant radiocarbon date

with a possible reservoir effect. While sample 416 also has a $\delta^{15}N$ value of 8.3‰, its date suggests a minimal or even no reservoir effect. Vice versa, sample 87, though having a light $\delta^{15}N$, also yielded a deviating radiocarbon date with a possible reservoir effect.

Charred residues 3, 279, 291 and 440 all show a radiocarbon date with a possible reservoir effect but no C20:3 ω-o-alkylphenyl alkanoic acid was found with GC-MS and the most remarkable is that food crusts 279 and 291 have $\delta^{15}N$ values lower than 5‰.

The presence of C20:3 ω-o-alkylphenyl alkanoic acid depends primarily on the type of fish. Half-lean and lean fish contain C20:3 n-3 fatty acids in the fish meat while none were detected in oily fish (Castro-Gonzalez 2007). Burnt bones of cyprinids were excavated in Doel and cyprinids can be categorised under half-lean and lean fish. Olsson and Isaksson (2007) noted during their decomposition experiments that the lean marine fish did not produce C20:3 alkanoic acid in substantial amounts. Freshwater fish, as excavated in Doel, have even lower contents of polyunsaturated fatty acids than saltwater fish (Vlieg and Body 1988, 151). Moreover C20:3 alkanoic acids are also present in the muscle, liver and adipose tissues of Iberian and white pigs (Estévez et al. 2004, 453-461) and in the fat and muscles of a feedlot steer (Sweeten et al. 1990, 43-45). But also the raw lean meat of beef, veal, lamb, mutton and chicken contains C20:3 n-6 fatty acid while raw flathead and canned red salmon had none (Food Standards Australia New Zealand 2006). Comparison of wild ruminant and cattle muscle tissues shows that the percentage of polyunsaturated fatty acids in wild ruminants is substantially higher than that in domesticated animals (Crawford, Woodford and Casped 1970; Miller et al. 1986). The observation of C20:3 ω-o-alkylphenyl alkanoic acid in the food crusts of Doel may therefore be evidence for wild boar and deer consumption.

5. Conclusion

The detection techniques for aquatic products evidence in food crusts are not fully reliable. Until there is a foolproof and reliable technique to detect aquatic compounds in charred residues, food crusts dates should be treated with extreme caution.

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